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Evaluation of Sorbents and Additives for
Dry SO₂ (Sulfur Dioxide) Removal

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ABSTRACT

Bench scale reactivity studies of alkaline sorbents were performed in an integrated fixed bed reactor, simulating the fabric filter dust layer of dry FGD systems. Relative humidity significantly affected SO₂ absorption by lime and limestone plus additives such as CaCl₂, Ca(NO₃)₂, and NaNO₃; but had less impact on NaHCO₃ reactivity. Different reaction patterns of various sorbents were observed. Results are discussed relating to sorbent screening for dry FGD systems.

INTRODUCTION

The increased interest in dry flue gas desulfurization (FGD) processes for removal of sulfur dioxide (SO_2) over the last 5-10 years (specifically, the perceived need for testing, evaluating, and comparing various sorbents) has spurred the development of bench-scale apparatus to study specific FGD reactions prior to actual pilot-scale testing (1-7). Some researchers used a differential reactor for studying the reaction kinetics; others used an integral sand bed reactor for measuring the initial rate of reaction of SO_2 with sorbent. The present work also uses a sand bed reactor for studying the reaction of gaseous SO_2 with solid sorbent, similar to an alkaline dust cake on a fabric filter with SO_2 -laden flue gas passing through it. Changes in gas phase and sorbent composition during the reaction are included in the present study as they are believed to play a significant role for any industrial application.

Sorbents investigated in this work included hydrated limes, sodium bicarbonate, and limestone. Various sorbent qualities, particle sizes, and sorbent additives were tested. While performance comparisons between the various sorbents are emphasized, some reaction rate controlling models for relating performance differences between the various sorbents are also proposed and discussed.

EXPERIMENTAL APPARATUS AND TESTING FEATURES

The experimental apparatus shown in Figure 1 was developed using recommendations from other research groups performing similar studies (e.g., Gary T. Rochelle's group at the University of Texas) and from experience gained in initial tests stressing data quality and data repeatability. The core of the experimental apparatus is the sand bed reactor where the SO_2 in the test gas reacts with the alkaline sorbent. The sand bed

reactor is a vertical packed bed of approximately 1 g sorbent dispersed in (normally) 40 g inert silica sand; the entire bed is supported on a 4.5 cm diameter fritted glass plate contained in a glass cylinder. The simulated flue gas passes down through the sand bed at a face velocity of up to 6 cm/s.

The three process variables expected to influence the SO_2 capture by the sorbent are: the SO_2 concentration in the simulated flue gas, the dry bulb temperature of the gas, and the relative humidity.

In the present work, it was decided to use pure nitrogen for simulating the dry flue gas composition: data from Rochelle indicated no effects of oxygen and carbon dioxide on SO_2 absorption in the sand bed reactor. While separate injection of SO_2 gas into the nitrogen gas stream is possible, the need for very accurate control of small gas flows dictated the use of commercially available calibrated span gases of SO_2 in nitrogen (SO_2 concentration range of 500 - 2000 ppm) as the test gas.

The desired temperature range of 54-85°C (130-185°F) was obtained by heating the test gas prior to its entering the reactor and immersing the entire reactor vessel in a thermostated water bath.

Since a broad range of moisture content in the flue gas was needed for testing, water was continuously and accurately injected using a syringe type dispensing pump, equipped with two syringes to allow continuous operation with transient-free switchover periods. Steady evaporation was achieved using a separate hot evaporation chamber (sand reservoir heated to 150-200°C (approx. 300-400°F)) prior to mixing the vapor with the test gas. A "back-mix chamber" in the water-bath-heated section of the apparatus ensured uniformity of the gas mixture entering the sand bed reactor.

The dry bulb temperature was measured just above the sand bed reactor. The exact wet bulb temperature was measured just downstream of the reactor using a wetted wick thermometer. The difference between dry and wet bulb temperatures

is the "approach to saturation," Δt_s , which together with the pressure measurement (U-tube manometer) establishes the relative humidity at test conditions. Measurement of the water injection, water collection, and gas flow rates permitted calculation of gas humidity and served as a quality control check on this important test parameter.

Prior to testing, the sand bed reactor was by-passed, and the test gas SO_2 concentration was established with a DuPont 411 SO_2 analyzer by comparison with a standard of higher SO_2 concentration (normally up to 3000 ppm). The water injection/condensation system was normally operated during the SO_2 calibration procedure. Water/ SO_2 equilibrium data (8) suggest that any SO_2 capture by the condensed water would amount to less than 2 - 3 percent of the total amount of SO_2 in the gas phase. This was confirmed by repeated comparisons of SO_2 analyzer data using dry gas calibration followed by calibration with water injection/condensation operation. During testing the gas passed from the sand bed reactor via the water condensation system to the SO_2 monitor, and SO_2 absorption in the sand bed reactor was established by integration of the recorded SO_2 concentration/time curve.

SAND BED REACTOR MODEL

Work by others (5) suggests that satisfactory dispersion of sorbent in the sand bed (i.e., good mixing and little agglomeration of sorbent particles) seems to be achieved when using 40 g sand per 1-2 g sorbent. The satisfactory repeatability of results obtained in the present work seems to support this assumption. The sand bed containing the alkaline sorbent is of cylindrical shape (approximately 4.5 cm in diameter and 1.6 cm in length when using 40 g sand). Supplier specification of the sand (Ottawa Industrial Sand Co., Grade F-70) and independent measurements indicate a bed voidage of $\epsilon = 0.40$. The intensity of dispersion can be estimated using the methods of Levenspiel (9) for

calculation of the Reynolds, Re, and Schmidt, Sc, numbers normally used in the tests:

$$Re = \frac{d_p u \rho}{\mu} = \frac{(1.4 \times 10^{-2}) \times (6.3) \times (1.0 \times 10^{-3})}{190 \times 10^{-3}} = 0.5 \quad (1)$$

$$Sc = \frac{\mu}{\rho D_{SO_2}} = \frac{190 \times 10^{-3}}{(1.0 \times 10^{-3}) \times (0.156)} = 1.2 \quad (2)$$

where d_p = particle diameter, cm ρ = gas density, g/cm³
 u = face velocity, cm/s μ = gas viscosity, g/cm-s
 D_{SO_2} = SO₂ molecular diffusion coefficient, cm²/s

Using the chart in Reference 9 for a plug-flow fixed-bed reactor with $\epsilon = 0.40$ gives a dispersion coefficient, D, of 0.132. From the above data for the sand bed, the dispersion number becomes:

$$\frac{D}{u L} = \frac{0.132}{(6.3) \times (1.6)} = 0.013 \quad (3)$$

where L is the height of sand bed reactor in centimeters.

This low dispersion number suggests that the effects of mixed flow probably can be disregarded and that a plug flow model is a reasonable assumption.

The accepted model for this type of heterogeneous reaction is the unreacted core model in which the reaction starts at the outer skin of the particle, and the zone of reaction then moves progressively into the particle, leaving behind completely converted reaction products, or ash. Applying this model for the SO₂/sorbent reaction, the following three reaction steps are proposed, each of which potentially could control the overall rate of conversion of SO₂ with sorbent:

1. Diffusion of gaseous SO₂ to the surface of the solid particle.
2. Penetration and diffusion of SO₂ through the ash layer to the surface of the unreacted core.
3. Reaction of SO₂ with sorbent at the core reaction surface.

While the present test work does not aim to completely establish the system's reactions for different sorbents using any of the above mechanisms with related rate constants, such a model can be very helpful in interpreting and evaluating data. The difficulty in precisely determining any of the above mechanisms as the sole overall rate controlling step using data from the sand bed reactor is related to the semi-batch characteristics of the experimental apparatus (the SO₂ flow is continuous over a batch of sorbent), which increases the probability of having different mechanisms controlling the overall rate at different times.

Relative to the gas film diffusion step, the dispersion of the solid sorbent in an inert silica sand avoids both channeling and by-passing of the sorbent, enabling a uniform gas flow with well defined gas/solid contact. Assuming satisfactory dispersion of sorbent without significant agglomeration, the mass transfer number for SO₂ from the gas phase to sorbent surface can be estimated using the modified Reynolds number (8):

$$\bar{Re} = \frac{d_p u \rho}{\mu (1-\epsilon)} = \frac{(1.4 \times 10^{-2}) \times (6.3) \times (1.0 \times 10^{-3})}{(190 \times 10^{-3}) \times (0.60)} = 0.77 \quad (4)$$

Colburn's j-factor for mass transfer(8) is:

$$j_D = 5.7 \times (\bar{Re})^{-0.78} = 5.7 \times (0.77)^{-0.78} = 7.0 \quad (5)$$

Using the earlier calculated Schmidt number, the gas transfer number is:

$$k_g = j_D \frac{G}{M} Sc^{-2/3} = (7.0) \frac{(0.0137)}{(28)} (1.2)^{-2/3} = 3.0 \times 10^{-3} \text{ mol/cm}^2\text{-s} \quad (6)$$

where G = mass gas flow, g/cm²-s

M = gas molecular weight, g/mol

A gas transfer coefficient of 3.0×10^{-3} mol/cm²-s suggests a very fast mass transfer rate from gas to solid sorbent. Using the equation from Levenspiel(9) expressing time, τ , for complete reaction of a solid particle with a gas and assuming that gas film diffusion is rate controlling:

$$\tau = \frac{\rho_p R}{3b k_g C_{Ag}} = \frac{(0.03) \times (5 \times 10^{-4})}{3 \times 1 \times (3.0 \times 10^{-3}) \times (5 \times 10^{-4})} = 3.5 \text{ sec} \quad (7)$$

where ρ_p = sorbent particle molar density, for calcium hydroxide $[\text{Ca}(\text{OH})_2]$, mol/cm³

R = sorbent particle radius, cm

b = reaction stoichiometry for $\text{Ca}(\text{OH})_2$

C_{Ag} = bulk concentration of SO_2 in gas phase (for 500 ppm), mol SO_2 /mol gas

This example suggests that a 10 μm diameter hydrated lime particle would react totally with SO_2 in a few seconds if gas-phase diffusion were the overall rate controlling step. As the measured time for reaction is much longer (as will be seen, significant amounts of unconverted sorbent are found even after 1 hr reaction), gas film diffusion can probably be excluded as the overall rate controlling step. This result also indicates that the actual gas face velocity chosen would not impact the overall rate of reaction.

EXPERIMENTS AND RESULTS

Results Using Hydrated Limes as Sorbents

As the present test work compares performance between various sorbents and the effect of changing selected process conditions, a "baseline" sorbent and some standard operating conditions were chosen: 1 g of reagent grade $\text{Ca}(\text{OH})_2$ (Fisher C-97) dispersed in 40 g sand, the sand bed reactor operated at 64.4°C (148°F), and 325 l/h (approx. 10 scfh) nitrogen with 500 ppm SO_2 supplied to the reactor. A reference time of 1 hr was used for testing.

A typical SO_2 outlet concentration/time curve for a single run is shown in Figure 2. Zero outlet concentration was measured during the initial testing period, but later the SO_2 outlet concentration rises and approaches that of the inlet, indicating no further SO_2 absorption taking place in the reactor. The total amount of SO_2 absorbed during the run was found by integration of the area above the recorded curve, and comparison of the SO_2 absorbed with the amount

of Ca(OH)_2 initially present led to the conclusion that a significant amount of Ca(OH)_2 (60-90 percent) had not reacted with SO_2 . This result might be explained in terms of conventional theory as follows. Initially, no ash diffusion resistance exists, and all SO_2 reacts with fresh surface Ca(OH)_2 . Ash building up on the particle surface causes the reaction rate to decrease and the sand bed outlet SO_2 concentration to rise. Eventually the reaction ceases, and the SO_2 outlet concentration equals the inlet concentration, which corresponds to the ash diffusion resistance having reached an extremely high value. "Blinding" of the sorbent surface is probably a better description of this phenomenon.

Figure 3 depicts the amount of sorbent converted with SO_2 (mol SO_2 /mol Ca(OH)_2 present) after 1 hr for different relative humidities. Although no definite proof can be given at this point, it seems that the ash diffusion resistance, being the most probable mechanism stopping the reaction ("blinding"), is strongly related to relative humidity in the gas phase, probably via water adsorption on the particle. An important implication of this "blinding" of the sorbent surface is that the total conversion cannot be increased by increasing the SO_2 partial pressure in the gas phase. This was confirmed by tests using 1000 ppm SO_2 as shown in Figure 3.

Figure 4 shows the effect of temperature on SO_2 absorption. It appears that the conversion of Ca(OH)_2 with SO_2 increases somewhat with temperature for constant relative humidity, the order of magnitude is 20-30 percent per 10°C (18°F).

Some commercially available pressure hydrated limes have also been tested in the sand bed reactor. The results, shown in Figure 5, revealed somewhat lower SO_2 absorption by these hydrates in the range from 50 percent relative humidity, $\Delta t_5 = 13^\circ\text{C}$ (24°F), to 70 percent relative humidity, $\Delta t_5 = 7^\circ\text{C}$

(12°F), than by reagent grade Ca(OH)_2 . Using the BET surface area to compare results achieved in the sand bed reactor, a correlation between surface area and SO_2 absorption can be seen for the dolomitic samples, but none is apparent for the few calcitic types, based on these data.

Some inorganic salts were also tested as additives to reagent grade Ca(OH)_2 : calcium chloride (CaCl_2), sodium chloride (NaCl), sodium hydroxide (NaOH), and sodium nitrate (NaNO_3). The results of these tests are depicted in Figure 6. Each was mixed with Ca(OH)_2 in a dry procedure, and not by the procedure of water dissolution and mixing with sorbent followed by drying, as done by others (6, 7). The outlet SO_2 concentration/time curves were similar to those described above for pure Ca(OH)_2 , but all additives shifted the ultimate SO_2 absorption somewhat. Continuing what was said earlier, this would indicate that the additive changes the ultimately controlling SO_2 ash "blinding" effect correspondingly. The most notable result is probably the quite significant increase in SO_2 absorption using CaCl_2 as additive. Relating to an earlier statement regarding water adsorption on the lime particles, it is believed that the CaCl_2 , having a high water affinity ("hygroscopic salt"), increases the water absorbed by the particle, thereby reducing the SO_2 ash "blinding" effect.

Results Using Sodium Compounds as Sorbents

Most bench-scale studies using sodium compounds as dry sorbents for SO_2 removal have been performed at temperatures in the range 150-250°C (300-500°F) (1). Sodium bicarbonate, NaHCO_3 , which has been extensively studied, thermally decomposes to anhydrous soda ash at these temperatures, which has often been claimed to be an important factor in the SO_2 removal process. The present work, however, focuses on the reactions at a lower temperature, 64.4°C (148°F), where the effect of thermal decomposition of

NaHCO_3 is expected to be less significant. To investigate thermal decomposition effects, some comparison tests were done using different time periods for "conditioning" sorbent samples (at test conditions of temperature and humidity) prior to exposure to the SO_2 test gas. Subsequent testing, however, gave the same SO_2 absorption results, independent of differences in time periods for "conditioning."

A typical SO_2 concentration/time curve as recorded by the SO_2 monitor using reagent grade (Fisher S-233) NaHCO_3 as sorbent in the sand bed reactor is shown in Figure 7. It appears that a steady SO_2 removal rate is established within a few minutes of sorbent exposure to SO_2 . This nearly constant rate, or constant SO_2 removal efficiency, is maintained throughout the testing period, being reduced only slightly with the gradual consumption of sorbent. This is entirely different from what was observed above using Ca(OH)_2 as sorbent (Figure 2).

A series of tests at different relative humidities showed somewhat increased SO_2 absorption with increased humidity. Also, tests were made using different amounts of NaHCO_3 in the sand bed and different SO_2 concentration levels. To help interpret these results, a plug flow reactor model was adopted for which the performance equation is (9):

$$\tau = C_{\text{SO}_2}^o \int_0^{x_{\text{SO}_2}^f} \frac{dx_{\text{SO}_2}}{-r_{\text{SO}_2}} \quad (8)$$

where τ = space time = $\frac{V\epsilon}{v_o}$, h

V = sand bed volume, ml

ϵ = sand bed voidage, fraction

v_o = gas volumetric flow, mol/h

$C_{\text{SO}_2}^o$ = inlet SO_2 concentration, mol/l

x_{SO_2} = conversion of SO_2 , fraction

$x_{\text{SO}_2}^f$ = outlet conversion of SO_2 , fraction

$-r_{\text{SO}_2}$ = rate of disappearance of SO_2 = $\frac{-dC_{\text{SO}_2}}{dt}$, mol/l-h

If the reaction rate is expressed as a first order reaction in both sorbent and SO_2 , then:

$$-r_{\text{SO}_2} = k C_{\text{sorb}} C_{\text{SO}_2} = k \frac{N_{\text{sorb}}}{V (1-\epsilon)} C_{\text{SO}_2}^0 (1 - X_{\text{SO}_2}) \quad (9)$$

where k = a rate constant for the reaction, l/mol-h

C_{sorb} = concentration of sorbent in the sand bed, mol/ml

N_{sorb} = amount of sorbent in the sand bed, mmol

As the total amount of sorbent is fairly large, compared to the amount reacted during the reaction period of interest, assume:

$$N_{\text{sorb}} = N_{\text{sorb}}^0 \text{ (initial amount of sorbent)}$$

Inserting these expressions in the performance equation (Eq. 8) and expressing the sorbent as sodium oxide, Na_2O , yields:

$$\tau = \frac{V\epsilon}{v_o} = \frac{V (1-\epsilon)}{k N_{\text{Na}_2\text{O}}^0} \int_0^{X_{\text{SO}_2}^f} \frac{dX_{\text{SO}_2}}{1-X_{\text{SO}_2}} = \frac{V (1-\epsilon)}{k N_{\text{Na}_2\text{O}}^0} (-\ln (1-X_{\text{SO}_2}^f)) \quad (10)$$

Rearranging,

$$-\ln (1 - X_{\text{SO}_2}^f) = k \frac{\epsilon}{v_o (1-\epsilon)} N_{\text{Na}_2\text{O}}^0 \quad (11)$$

The left side of Equation 11 has been plotted versus $N_{\text{Na}_2\text{O}}^0$ for all test runs using NaHCO_3 as the sorbent and is depicted in Figure 8. In the low humidity range, the slopes of the linear curves indicate the rate constant, k , of 8, 18, and 25 l/mol-h , almost proportional to the corresponding relative humidities of 15, 30-35, and 45-50 percent, respectively. For higher relative humidity, 70-75 percent, interpretation of the results seems more complex in terms of the above equation; the plot reveals the same straight line slope as was observed at 50 percent relative humidity. Even at the quite high SO_2 absorption rates (at high humidity, the measured range covers 40-75 percent steady state SO_2 removal across the sand bed reactor), however, no reaction inhibiting effects

such as "blinding" were seen. A probable mechanism could be the CO_2 released during reaction with SO_2 creating sufficient fresh surface of sorbent to account for the continued reaction.

A few test runs were also made using reagent grade anhydrous sodium carbonate, Na_2CO_3 , (Fisher S-263) as sorbent. However, very low SO_2 absorption (less than 5 percent of that seen when using NaHCO_3), even at high relative humidity, was observed in the sand bed reactor, and no steady removal rate could be detected. Based on these data, it seems that the above reported fast reaction between SO_2 and NaHCO_3 at 64.4°C (148°F) proceeds without any intermediately formed anhydrous Na_2CO_3 .

Figure 9 depicts the SO_2 absorption achieved in the sand bed, expressed as conversion of Na_2O , after 1 hour, as a function of the relative humidity using various NaHCO_3 samples as sorbents. The difference in results between the various samples of NaHCO_3 is noteworthy, and is probably related to differences in surface area or other particle characteristics. However, a measurable quantity identifying these differences seems needed.

In summary, the relative humidity is less critical to SO_2 absorption by NaHCO_3 at low temperature than is $\text{Ca}(\text{OH})_2$. The reaction seems to be first order with respect to both SO_2 and sorbent. Based on what has been observed here, a mechanism involving the release of CO_2 during the reaction of SO_2 with NaHCO_3 seems best to explain the high reactivity of NaHCO_3 without any "blinding" effects.

Results Using Calcium Carbonate as Sorbent

Tests using pure reagent grade calcium carbonate, CaCO_3 , (Fischer C-64) and gas relative humidities in the range 40 - 70 percent (Δt_s approx. $17 - 7^\circ\text{C}$ ($30 - 12^\circ\text{F}$)) revealed no SO_2 absorption in the sand bed reactor. SO_2 absorption by limestone under dry conditions has been reported by others to be

enhanced by use of deliquescent salt additives, specifically CaCl_2 (5, 6). The additive enhancement of the sorbent has usually been done by mixing the sorbent with an aqueous solution of the additive followed by drying of the mixture. In the present work, however, the sorbent and additive were mixed dry to exclude any effect of specific sorbent pretreatment on the results obtained in the sand bed reactor.

The additive $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was mixed with the sorbent CaCO_3 in the amounts of 0.1 and 0.2 g, respectively, per 1 g sorbent. The effect of the additive on the SO_2 absorption measured in the sand bed was significant. Adding $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to CaCO_3 in the amount of 0.1 g/g (approx. 7 mol percent) resulted in the definite reaction of SO_2 with CaCO_3 at 70 percent relative humidity (about 0.1 mol SO_2 /mol CaCO_3 after 1 hr); however, using 0.2 g/g (approx. 13.5 mol percent) resulted in a SO_2 absorption at a magnitude similar to that observed earlier using pure reagent grade $\text{Ca}(\text{OH})_2$ at the same conditions (about 0.2 mol SO_2 /mol CaCO_3 after 1 hr). These results become even more noteworthy as the reaction of SO_2 with CaCO_3 gave a constant SO_2 removal efficiency across the sand bed throughout the testing period, similar to that described above using NaHCO_3 as sorbent (Figure 7), but different from that seen with $\text{Ca}(\text{OH})_2$ (Figure 2). These observations indicate that the significant reaction inhibiting effect with sorbent conversion ("blinding") which was assessed earlier using $\text{Ca}(\text{OH})_2$ as sorbent, does not seem to exist using CaCl_2 -enhanced limestone. The reaction is constantly proceeding, its rate decreasing only with the depletion of CaCO_3 sorbent.

A test matrix using 0.2 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ per 1 g CaCO_3 and 70 percent relative humidity at 64.4°C (148°F) was performed with varying inlet SO_2 concentration, amount of CaCO_3 sorbent, and amount of sand as test parameters. The results, depicted in Figure 10, suggested that:

1. SO₂ absorption increases proportionally with the amount of sorbent.
2. SO₂ absorption increases with the SO₂ concentration up to approximately 1000 ppm for most conditions tested.
3. The amount of sand used in the bed does not have any significant impact on the amount of SO₂ absorbed. (Only at the conditions where the SO₂ concentration and sorbent amount were at their maximums might an impact of the total quantity of sand also be detectable.)

These results do not support a single mechanism as rate controlling for SO₂ removal at the different test conditions.

Relative humidity is very critical to the degree of SO₂ removal which is achievable (also explaining some scatter observed in the above results). Lowering the relative humidity from 70 percent (Δt_s approx. 7°C (12°F)) to 50 percent (Δt_s approx. 13°C (24°F)) stops virtually all reaction of SO₂ with CaCO₃. Raising the dry bulb temperature from 64.4°C (148°F) to 74.4°C (166°F) also rapidly decreases the SO₂ removal, corresponding to lowering the relative humidity from 70 to 50 percent. Only by raising the wet bulb temperature correspondingly to restore the relative humidity could high SO₂ absorption be maintained (Figure 11).

In summary, the theory of a deliquescent salt, CaCl₂, generating a liquid phase for SO₂ reaction with CaCO₃ (5) agrees well with test results noted here. These results imply that a steady state SO₂ removal rate can be maintained across the sand bed reactor, unlike the reaction of SO₂ with Ca(OH)₂ where the reaction rate decreased with time ("blinding").

A few tests performed using NaCl instead of CaCl₂ as an additive to limestone revealed no reaction between SO₂ and CaCO₃. In terms of the

above conclusion, this would indicate that the less hygroscopic NaCl (i.e., less affinity for water) does not generate sufficient liquid phase on the particle surface for the dissolution and reaction of CaCO_3 with SO_2 .

Several commercial limestones [Fredonia (Kentucky) and aragonite] have been tested with CaCl_2 as the additive and samples of two different particle sizes (all particles minus 325 mesh or all particles in the range 200-325 mesh). The results shown in Figure 11 portray the minus 325 mesh sample of Fredonia (a calcite) to react somewhat faster with SO_2 at 70 percent relative humidity than did reagent grade CaCO_3 . This might be attributed to the higher specific surface area of the finer particles. For aragonite a significantly higher SO_2 absorption rate occurred than for either of the tested calcites: the difference was probably related to the different crystal structure or surface shape. Significant SO_2 was also removed with aragonite at lower relative humidity (40-50 percent relative humidity, Δt_s approx. 17-12°C (30-22°F)), especially with the fine particulate fraction (minus 325 mesh) sample of sorbent. Results of a few tests using aragonite without additive enhancement are also presented in Figure 11. Clearly, some SO_2 absorption was achieved at high relative humidity, which seems to confirm that the specific sorbent crystal or surface characteristics might be as important for high SO_2 removal as the increased liquid phase obtained by addition of a deliquescent salt.

The last test series to be reported here used sodium nitrate, NaNO_3 , and calcium nitrate, $\text{Ca(NO}_3)_2$, as additives to reagent grade CaCO_3 sorbent, and also revealed quite high SO_2 absorption in the sand bed when operating at high relative humidity (70 percent relative humidity, Δt_s approx. 7°C (12°F)). Moreover, use of both additives revealed a constant SO_2 removal across the sand bed throughout the testing period, similar to that described above for CaCl_2

added to CaCO_3 . A "blank" test using only NaNO_3 in the sand bed showed no absorption of SO_2 at similar conditions, suggesting that only a reaction between SO_2 and CaCO_3 , enhanced by the nitrate compound, could explain the results. The results of a small test matrix aimed at evaluating the effects of the amount of additive used and the SO_2 concentration are shown in Figure 12. Surprisingly, these results showed that, for given test conditions, there seems to be an optimum ratio of additive to sorbent for maximum absorption of SO_2 by CaCO_3 . Recalling the previous discussion of a liquid phase on the particle surface, this indicates that a specific ratio of SO_2 to NO_3^- in the liquid phase results in the highest dissolution rate for CaCO_3 . While this effect cannot be explained at this point, it is noted that a similar " SO_x/NO_x ratio" has been reported to play a role for simultaneous SO_x/NO_x removal in a spray dryer/baghouse process (10).

The SO_2 conversion achieved in the sand bed in tests using nitrate additives could show some effect of the time used for "conditioning" the sorbent sample. Also, an increasing SO_2 removal efficiency across the sand bed during the testing period could sometimes be observed. These observations suggest that a time factor related to achievement of equilibrium for this specific system might be of importance for the reaction performance.

Finally, some tests with relative humidity and dry bulb temperature as parameters for the CaCO_3 /nitrate system were also made, but the results were similar to those observed with CaCl_2 added to CaCO_3 . Thus, the relative humidity (or approach to saturation), not the actual temperature, seems to control the SO_2 absorbed in the sand bed.

CONCLUSIONS

- o The sand bed reactor has been developed as a useful tool for studying dry sorbent reactions with SO_2 at low temperatures.
- o Hydrated limes react with SO_2 in the temperature range 55-75°C (130-166°F) with the conversion increasing markedly with the gas relative humidity. This agrees with pilot and full-scale dry scrubber test work showing SO_2 removal to increase with decreasing approach to saturation.
- o The lime conversion can be increased somewhat by using salt additives.
- o The SO_2 /lime reaction is inhibited with conversion of the sorbent, probably due to ash buildup on the particle surface ("blinding"). The implication is that a process using recycle of lime sorbent would require some "reactivation" to remove this ash layer to achieve high lime utilization.
- o Sodium bicarbonate efficiently absorbs SO_2 at 65°C (148°F), but the absorption increases less with increasing gas relative humidity than seen with Ca(OH)_2 sorbent. This indicates that a soda based dry scrubber would be less sensitive to changes in approach to saturation.
- o The reaction between SO_2 and NaHCO_3 proceeds without any "blinding." This suggests that very high sorbent utilization can be achieved on a soda based dry scrubber by increasing sorbent residence time in the gas stream.
- o Normal CaCO_3 does not react with SO_2 in the sand bed reactor, but the use of additives such as CaCl_2 , NaNO_3 , and $\text{Ca(NO}_3)_2$ significantly enhances the reaction at high relative humidity.
- o Higher SO_2 absorption can be achieved using fine particulate CaCO_3 as sorbent and by using aragonite instead of calcite.

- o The reactions of SO_2 with additive enhanced CaCO_3 do not indicate any "blinding" of sorbent with conversion.
- o These results suggest that CaCO_3 with additive can be used in lieu of hydrated lime in a dry scrubbing system when operating with a low approach to saturation. Increased residence time of sorbent in the fabric filter using dry recycle of sorbent or extending time intervals between cleaning cycles can be expected to lead to higher sorbent utilization.

REFERENCES

1. W. T. Davis and T. C. Keener: "Chemical Kinetic Studies on Dry Sorbents," DOE/FC/10184-1 (DE82012765), 1982.
2. J. Klingspor, A. Stromberg, H. T. Karlsson, and I. Bjerle: "Similarities Between Lime and Limestone in Wet-Dry Scrubbing," Licentiate Thesis, University of Lund, Sweden, 1983.
3. I. Bjerle, J. Klingspor, and H. T. Karlsson: "Sulfur Capture by Promoted Limestone," Presented at the 11th Annual Stack Gas Meeting, Paducah, Kentucky, October 1983.
4. J. Klingspor, H. T. Karlsson, and I. Bjerle: "A Kinetic Study of the Dry SO_2 -Limestone Reaction at Low Temperature," Chem. Eng. Commun., 22, 81-103, 1983.
5. H. T. Karlsson, J. Klingspor, M. Linne, and I. Bjerle, "Activated Wet-Dry Scrubbing of SO_2 ," APCA Journal, 33 (1), 23-28, 1983.
6. R. N. Ruiz-Alsop and G. T. Rochelle: "Effect of Deliquescent Salt Additives on the Reaction of Sulfur Dioxide with Dry $\text{Ca}(\text{OH})_2$," Preprint of paper presented at 189th ACS National Meeting, 88-97, 1985.
7. R. N. Ruiz-Alsop: "Reaction of SO_2 with $\text{Ca}(\text{OH})_2$," Proposal for Ph.D. Dissertation, Department of Chemical Engineering, The University of Texas at Austin, February 1984.
8. Perry and Chilton: "Chemical Engineers Handbook," Fifth Edition, McGraw-Hill, 1973.
9. O. Levinspiel: "Chemical Reaction Engineering," Second Edition, Wiley, 1972.
10. K. Felsvang, P. Morsing, and P. Veltman: "Acid Rain Prevention Thru New SO_x/NO_x Dry Scrubbing Process," in Proceedings: Eighth Symposium on Flue Gas Desulfurization, New Orleans, LA, November 1983, Volume 2, EPA-600/9-84-017b (NTIS PB84-223049), pp. 650-667, July 1984.

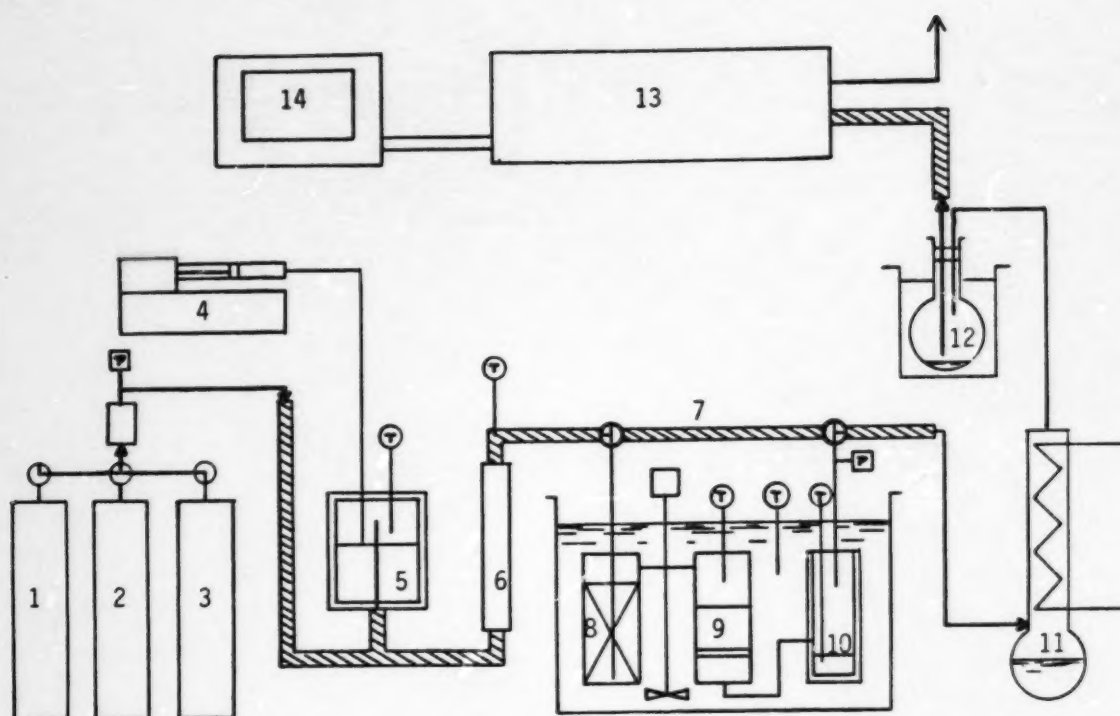


Figure 1: Experimental apparatus

- | | | |
|--------------------------|------------------------|------------------------------|
| 1. N ₂ supply | 5. Evaporation chamber | 9. Sand bed reactor |
| 2. Span gas | 6. Electrical heater | 10. Wet bulb thermometer |
| 3. Test gas | 7. By-pass line | 11. Condenser |
| 4. Syringe pump | 8. Back-mix chamber | 12. Water trap (ice) |
| | | 13. SO ₂ analyzer |
| | | 14. Recorder |

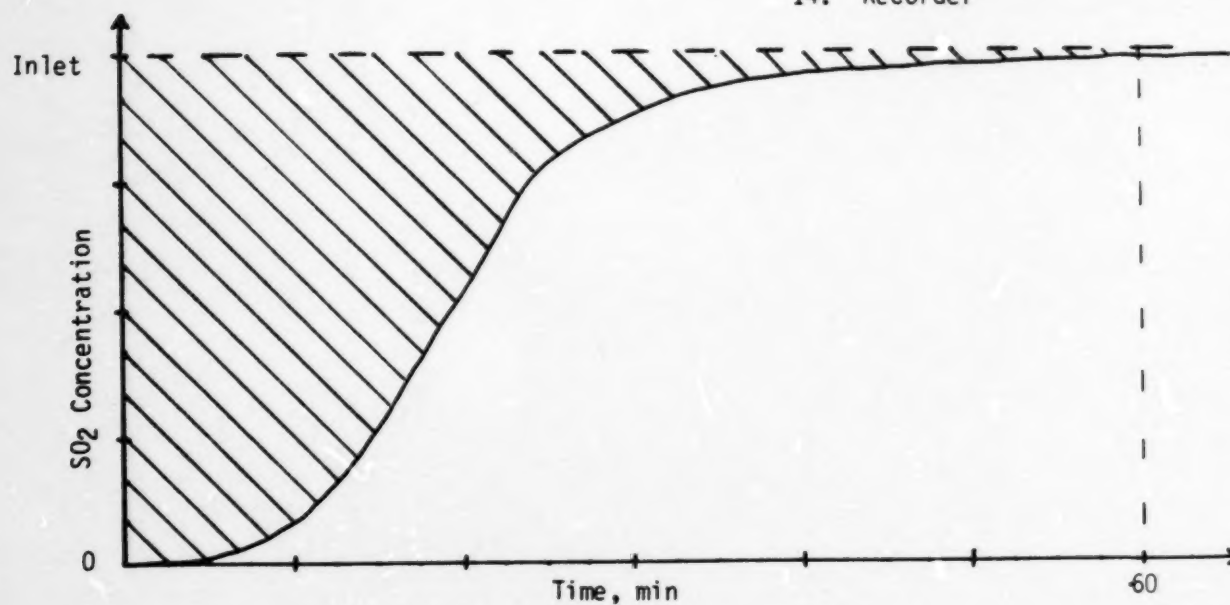


Figure 2: Generic strip chart from SO₂ analyzer using Ca(OH)₂ as sorbent in the sand bed

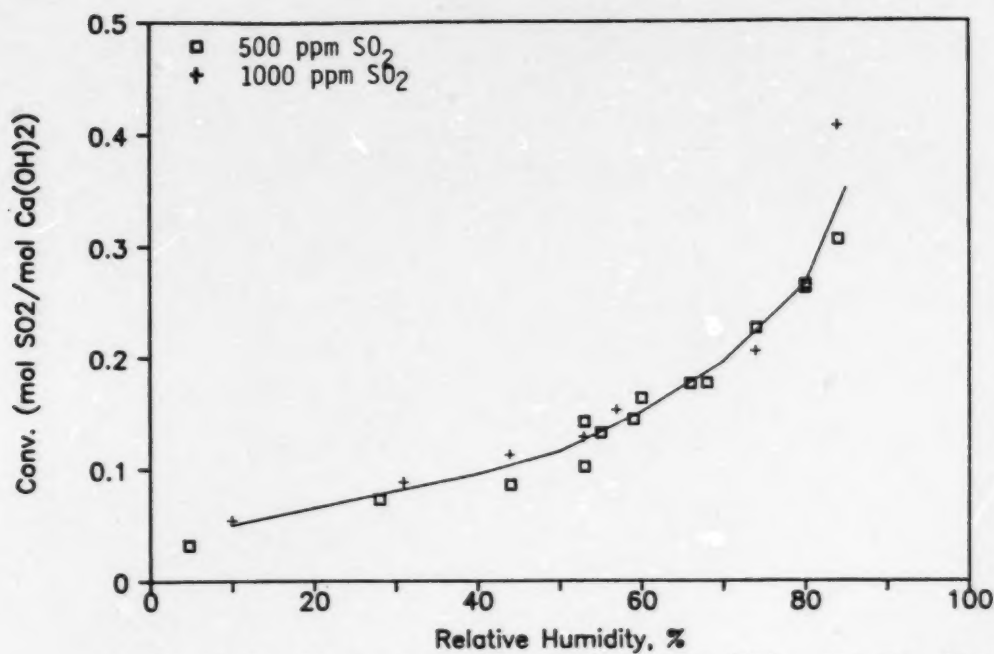


Figure 3: Conversion of reagent grade Ca(OH)_2 with SO_2 (1 hr)
1 g Ca(OH)_2 , 64.4°C (148°F)

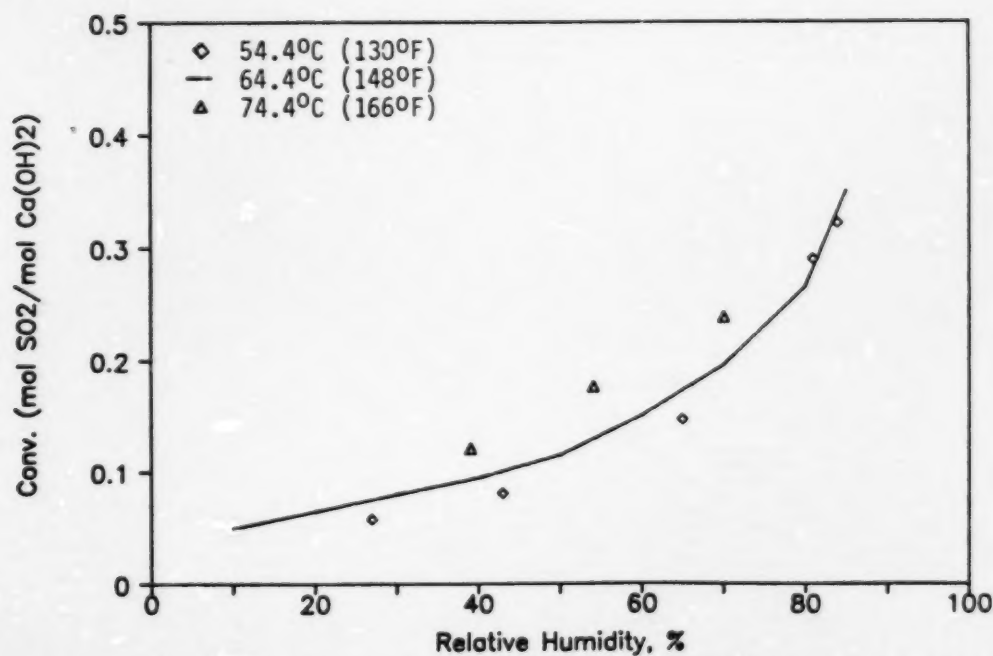


Figure 4: Conversion of reagent grade Ca(OH)_2 with SO_2 (1 hr)
1 g Ca(OH)_2 , 500 ppm SO_2

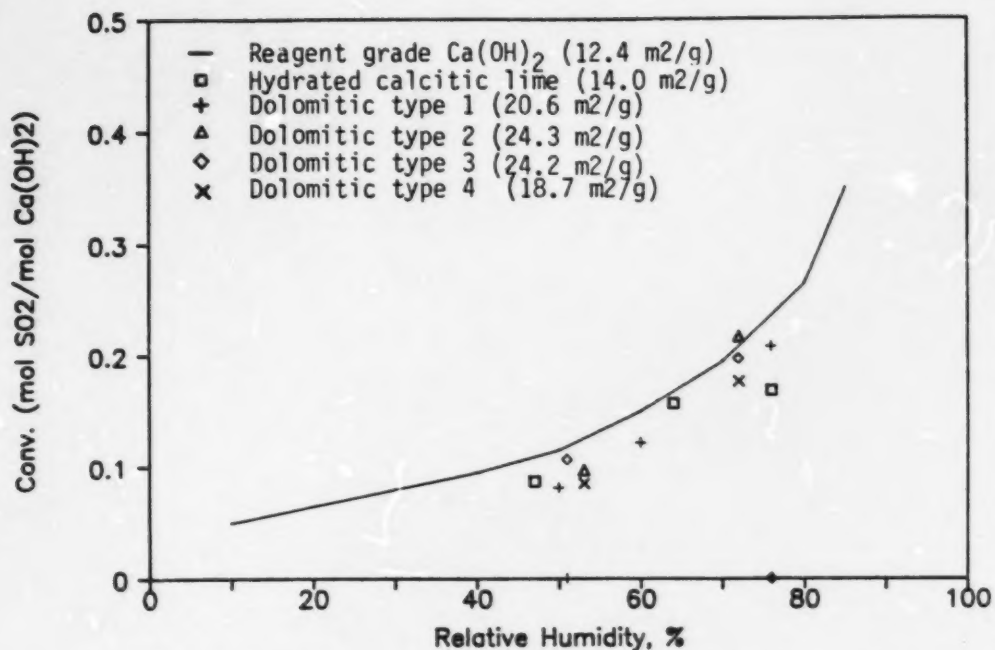


Figure 5: Conversion of different hydrated limes with SO_2 (1 hr)
1 g sorbent, 64.4°C (148°F), 500 ppm SO_2

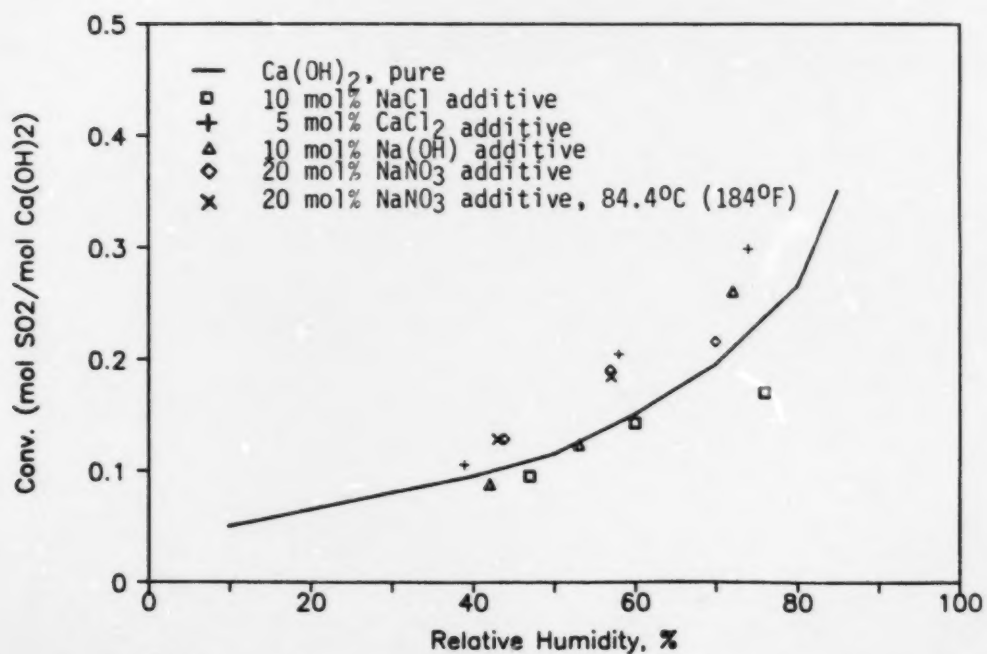


Figure 6: Conversion of Ca(OH)_2 + additives with SO_2 (1 hr)
1 g Ca(OH)_2 , 64.4°C (148°F), 500 ppm SO_2

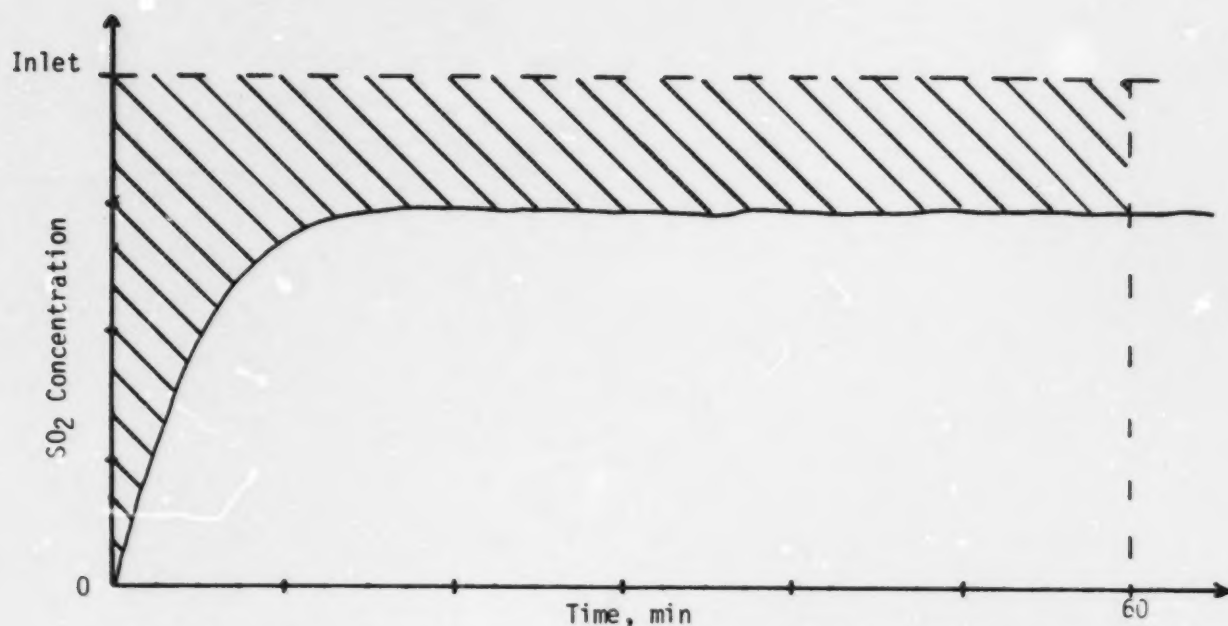


Figure 7: Generic strip chart from SO_2 analyzer using NaHCO_3 (or CaCO_3 + additive) as sorbent in the sand bed

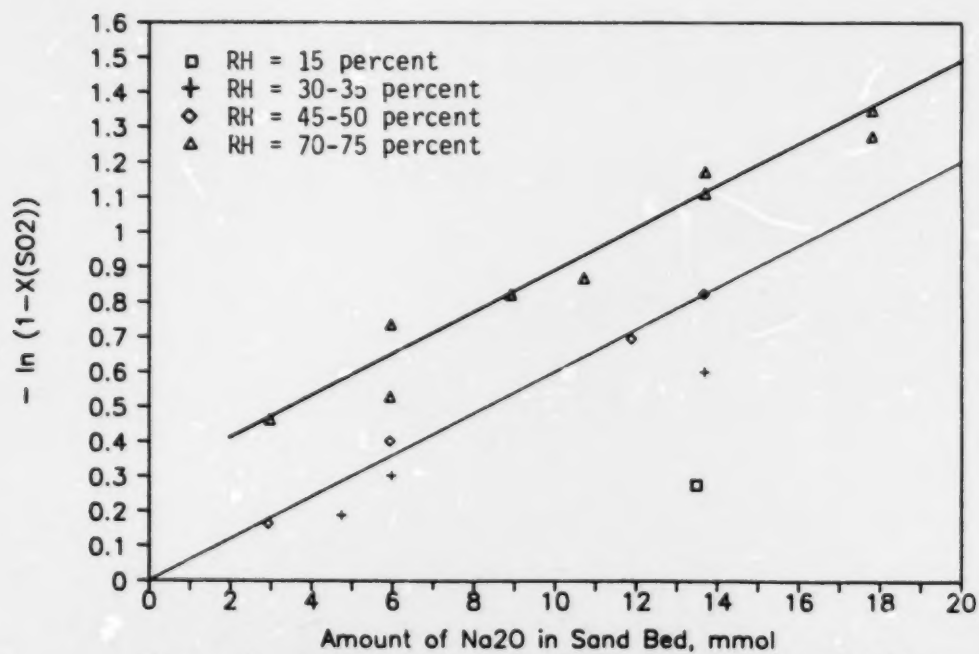


Figure 8: Logarithmic plot of SO_2 removal using NaHCO_3 as sorbent 64.4°C (148°F), 500-1000 ppm SO_2

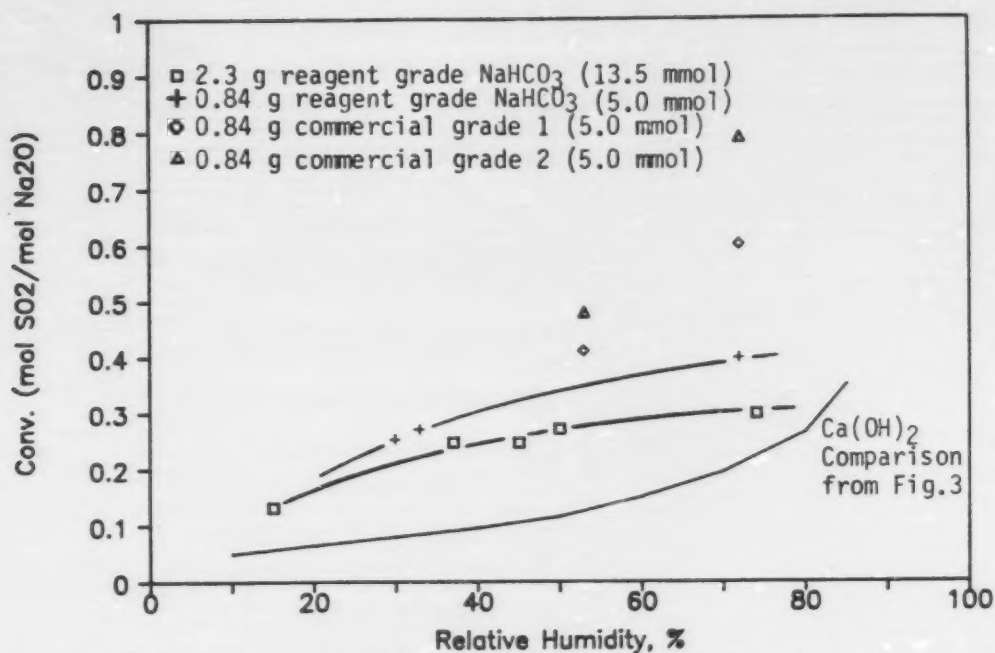


Figure 9: Conversion of NaHCO_3 with SO_2 (1 hr)
 64.4°C (148°F), 500 ppm SO_2

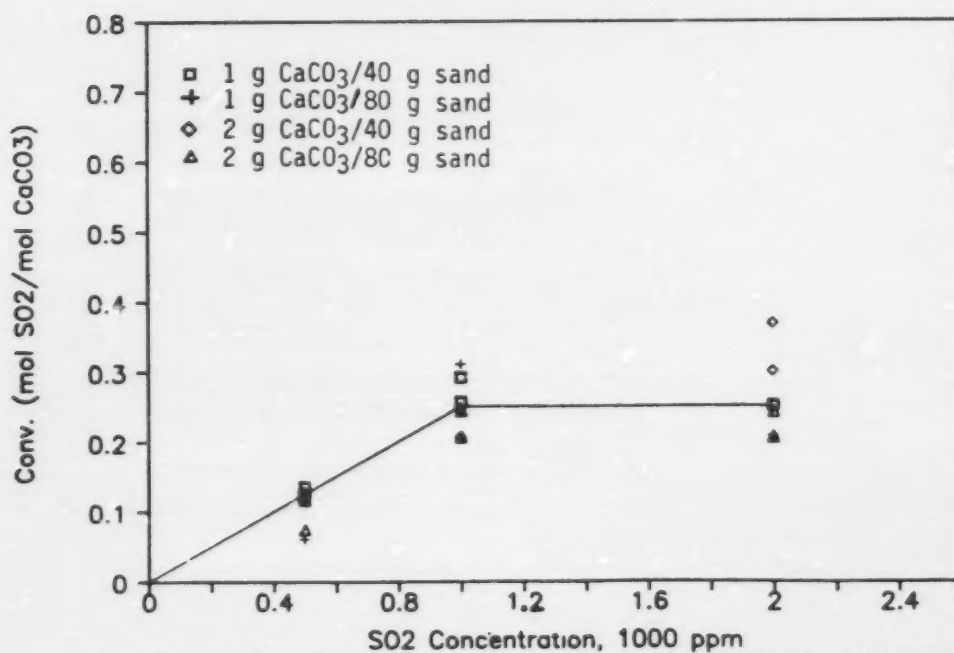


Figure 10: Conversion of chloride enhanced CaCO_3 with SO_2 (1 hr)
 $0.2 \text{ g CaCl}_2 \cdot 2\text{H}_2\text{O/g CaCO}_3$
 64.4°C (148°F), RH = 70 percent

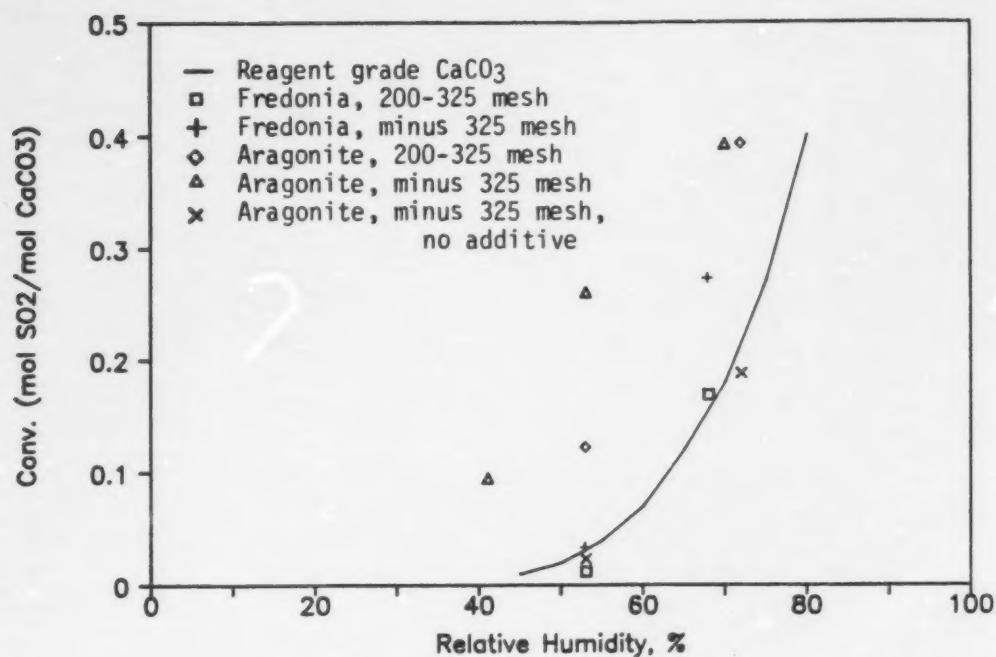


Figure 11: Conversion of various Cl enhanced CaCO_3 with SO_2 (1 hr)
 2 g CaCO_3 , 0.2 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ /g CaCO_3
 64.4°C (148°F), 1000 ppm SO_2

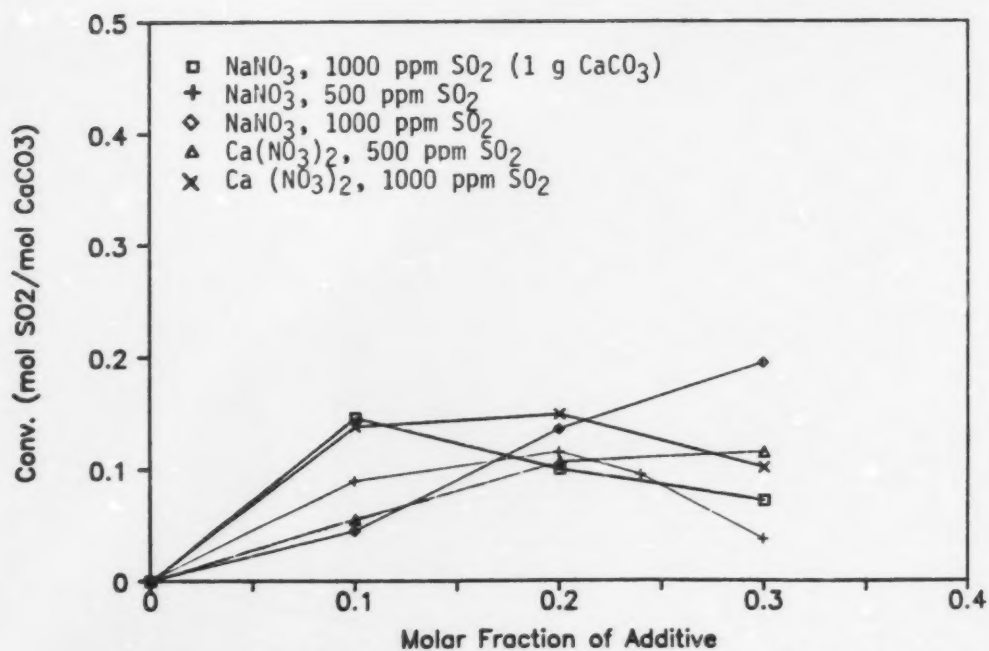


Figure 12: Conversion of nitrate enhanced CaCO_3 with SO_2 (1 hr)
 2 g CaCO_3 , 64.4°C (148°F), RH = 70 percent